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## **EVALUATION OF CURING BEHAVIOR OF TETRA- FUNCTIONAL EPOXY RESIN WITH METHYL NADIC ANHYDRIDE**

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### **ABSTRACT**

Tetra-functional epoxy resin has been synthesized, starting from 4,4'-diaminodiphenylether and epichlorohydrin. The curing behavior of synthesized epoxy resin has been evaluated using methyl nadic anhydride (MNA) as a curing material. The obtained resin was characterized by FT-IR and <sup>1</sup>HNMR spectroscopy. The curing behavior of epoxy resin with MNA has been studied using FT-IR and Differential scanning calorimetry (DSC) techniques. The thermal behavior of epoxy resin has been evaluated using Thermo gravimetric Analyzer (TGA) and DSC techniques. The DSC analysis of uncured resin with MNA showed the maximum rate of curing at 177 °C. The cured epoxy resin showed T<sub>g</sub> at 197 °C. The TGA analysis of cured epoxy resin showed two step degradation, T<sub>onset</sub> at 350 °C with char yield of 22% at 800 °C.

**Key Words:** Epichlorohydrin, Methyl Nadic Anhydride, Curing Agents, Thermo Gravimetric Analyzer.

### **INTRODUCTION**

Epoxy resins constitute a diverse family of polymers which may be formulated into elastomers, bonding agents, coatings and matrix formers. A precursor containing multiple epoxy groups is allowed to react with a co-reactant to form an additive crosslinked network. The diverse properties which may be engineered into epoxy resin systems find their origin in the chemical composition of the precursors which bear the epoxy groups and their co-reactants [1-4]. Epoxy resins are most versatile compounds, widely used for surface protective coatings, electric & electronic

insulating materials and composite matrices because the properties of the composites are primarily determined by the structure of matrix resins [5-6]. The epoxy resins show superior heat resistance, better adhesive properties and good mechanical properties. Intensive research efforts are currently going on to develop new epoxy resins with improved thermal and thermo-mechanical properties along with physical modification of the classical epoxy resins to enhance the desired properties [7-8]. Another approach to improve the properties of epoxy resins without sacrificing their useful properties, which is very important, is the choice of a suitable hardener [9].

Recently tetra-functional epoxy resins have been used as a matrix resin to developed high performance composite materials [10-11]. The conventional epoxy resins have failed to satisfy the desired properties like superior thermo-oxidative stabilities, high thermo-mechanical strength along with chemical and moisture resistance to be used for advanced composite material applications [12-13]. Various ways have been applied to enhance the thermal properties of the epoxy resins, either by the introduction of aromatic rings which can improve the heat resistance of epoxy resins or by increasing the number of functionalities of the epoxy resins which can enhance the thermal properties because of high curing density of cured epoxy resins [14]. Recently multifunctional epoxy resins have attracted extensive interest of researchers and Industrialist because of their use in Military and civilian sectors due to their highly cross linked structures, good thermal and mechanical properties [15-17].

The main aim of the present study is to report the curing behavior of a tetra-functional epoxy resin using methyl nadic anhydride (MNA) as a curing material and its characterization by FT-IR & DSC. The thermal properties of the cured resin have been evaluated by thermo gravimetric analysis.

## EXPERIMENTAL

4, 4'-diaminodiphenylether (DDE) and methyl nadic anhydride (MNA) were obtained from Aldrich and used as received. Epichlorohydrin, triethyl amine was purchased from across and used without any further purification.

## INSTRUMENTATION

A  $^1\text{H}$ NMR spectrum was recorded in  $\text{CDCl}_3$  on a 400MHz Bruker T spectrometer. FT-IR spectrum was recorded on a Perkin Elmer spectrophotometer using KBr as a reference material. The thermo gravimetric analysis was performed under nitrogen atmosphere on a TA instrument. The DSC graph was recorded on TA instrument.

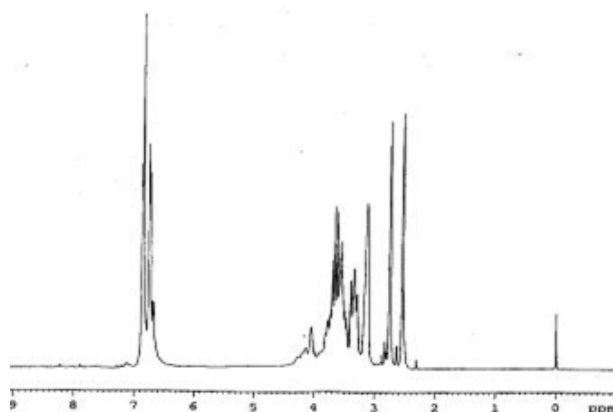
The synthesis of epoxy resin has been shown in scheme 1.

## SYNTHESIS OF TETRA-FUNCTIONAL EPOXY RESIN

To a 500ml three necked flask equipped with a reflux condenser under nitrogen atmosphere containing epichlorohydrin (100 ml) was added 4,4'-diaminodiphenylether (19.1g) and triethyl amine (40.4 g) gradually and the mixture was heated at  $65^\circ\text{C}$  for 6 hrs. The reaction mixture was cooled and distilled off to remove the excess of epichlorohydrin. The final viscous product was dried under vacuum oven at  $60^\circ\text{C}$  for over night.

$^1\text{H}$ NMR (Fig.1): 6.6-6.8ppm (two doublets, 8H) 2.5-3.8ppm (multiplet, 20H),

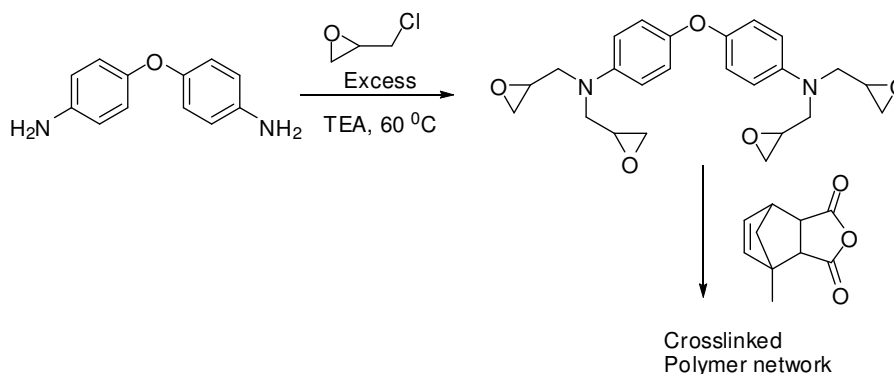
FT-IR (KBr  $\text{cm}^{-1}$ ) (Fig.1): 2968, 2927, 2873, 1609, 1510, 1460, 1362, 1245, 1033.



**Fig.1:**  $^1\text{H}$ NMR spectrum of synthesized epoxy resin

## CURING PROCEDURE OF EPOXY RESIN

The synthesized epoxy was cured with methyl nadic anhydride (MNA). The chemical structures of epoxy and curing agents are showed in scheme-1. The reactant compositions were mixed homogeneously in a 1:0.8 molar ratio for epoxy/anhydride system. The curing cycles were determined by DSC tracing of the respective epoxy/curing agent composition.



**Scheme-1:** Synthetic route of epoxy resin.

## RESULTS AND DISCUSSION

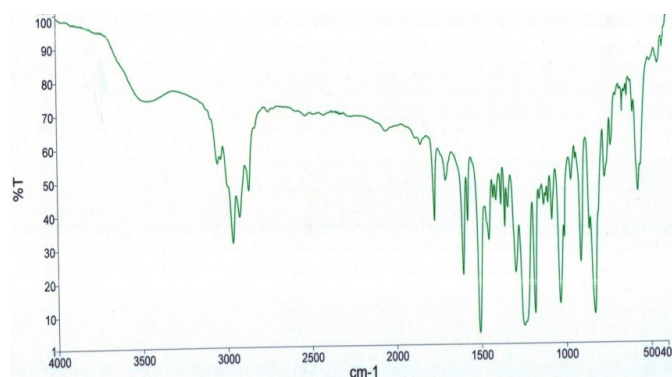
The tetra-functional epoxy resin has been synthesized by using a conventional method [14]. The formation of precursor material and its polymer have been confirmed by its FT-IR,  $^1\text{H}$ NMR spectroscopy, TGA & DSC.

## CURING ANALYSIS

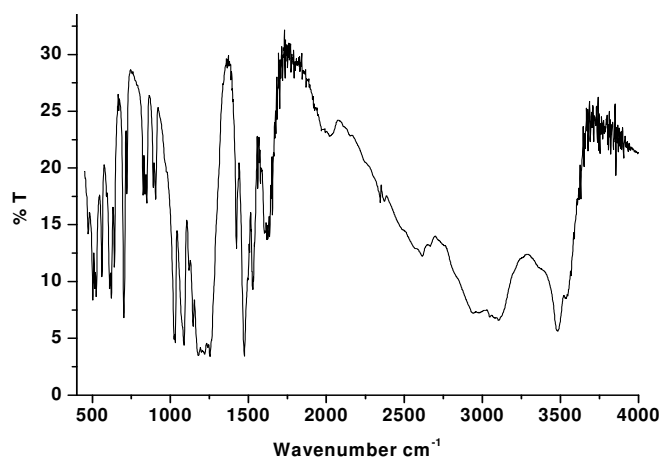
The curing analysis of tetra functional epoxy resin is evaluated by heating a mixture of 1:0.8 ratio of synthesized resin/MNA. At 100 $^{\circ}\text{C}$  for 1 hr, 125 $^{\circ}\text{C}$  for 2 hrs, 150 $^{\circ}\text{C}$  for 2 hrs, 175 $^{\circ}\text{C}$  for 2 hrs, 200 $^{\circ}\text{C}$  for 1 hr, 250 $^{\circ}\text{C}$  for 2 hrs, 300 $^{\circ}\text{C}$  for 2 hrs and 325 $^{\circ}\text{C}$  for 1 hr. No external curing accelerator has been added, as lone pair of N-atom of tetra functional epoxy resin itself acted as an initiator as shown in scheme 2.

## FT-IR ANALYSIS

The FT-IR spectrum of uncured epoxy/MNA resin (Fig. 2) showed the characteristic peak at  $1779.5\text{ cm}^{-1}$  corresponding to the stretching vibration of C=O (anhydride) linkage. The peak at  $3063\text{--}2873\text{ cm}^{-1}$  corresponding to =C-H and –C-H stretching vibrations. The peak at  $1609\text{ cm}^{-1}$  attributed to the aromatic C=C bond while the peak at  $1460\text{ cm}^{-1}$  which correspond to the characteristic peak of aromatic ring. The –C-O stretching of epoxide ring showed the characteristic peak at  $1033\text{ cm}^{-1}$ . The FT-IR spectrum of cured epoxy resin (Fig. 3) showed the characteristic broad peak at  $3500\text{ cm}^{-1}$  corresponding to the stretching vibration of the hydroxyl group of the free and hydrogen bonded -O-H group. The peak at  $1680\text{ cm}^{-1}$  correspond to the –C=O stretching. The peaks at  $1779.5\text{ cm}^{-1}$  which correspond to the stretching vibration of C=O (anhydride) linkage of uncured resin was not seen in FT-IR spectrum of cured epoxy resin which supported the formation of polymer network.



**Fig.2:** FT-IR spectrum of uncured epoxy resin.

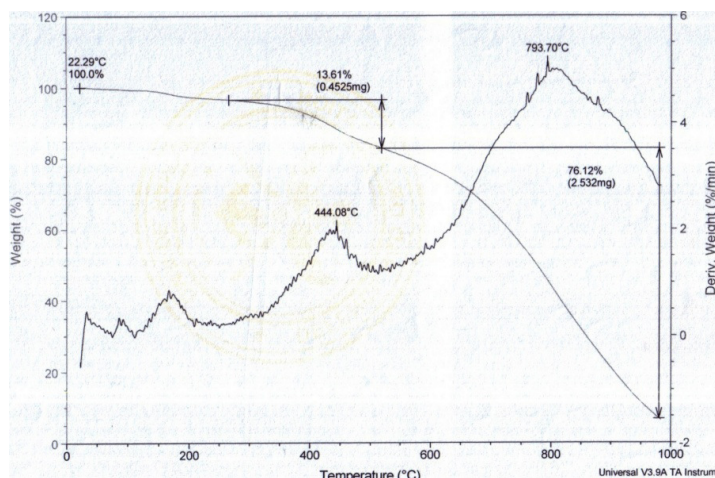


**Fig.3:** FT-IR spectrum of cured epoxy resin.

## THERMO-GRAVIMETRIC ANALYSIS

The TGA graph (Fig.4) of cured epoxy resin showed thermal stability of the tetra-functional epoxy resin up to  $350\text{ }^{\circ}\text{C}$  without any weight loss. The cured epoxy resin showed two step degradation patterns. The weight loss after  $350\text{ }^{\circ}\text{C}$  was probably due to degradation of aliphatic chains present in epoxy matrix. The maximum rate of decomposition of cured epoxy resin was observed at  $444\text{ }^{\circ}\text{C}$ . The weight loss at higher temperature of the cured epoxy resin was attributed

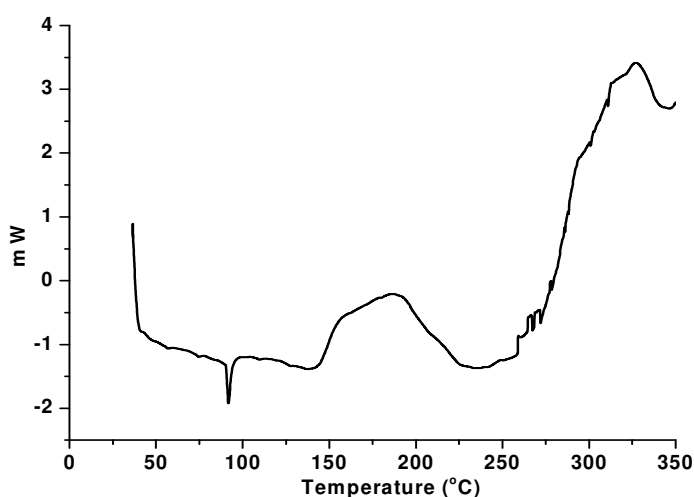
due to degradation of epoxy main chain. The endset degradation temperature of first step degradation was observed at 525 °C with char yield 22% at 800 °C.



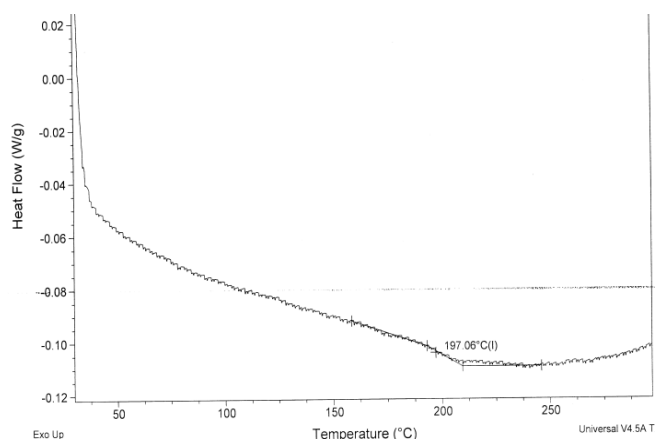
**Fig.4:** TGA graph of cured epoxy resin.

## DSC ANALYSIS

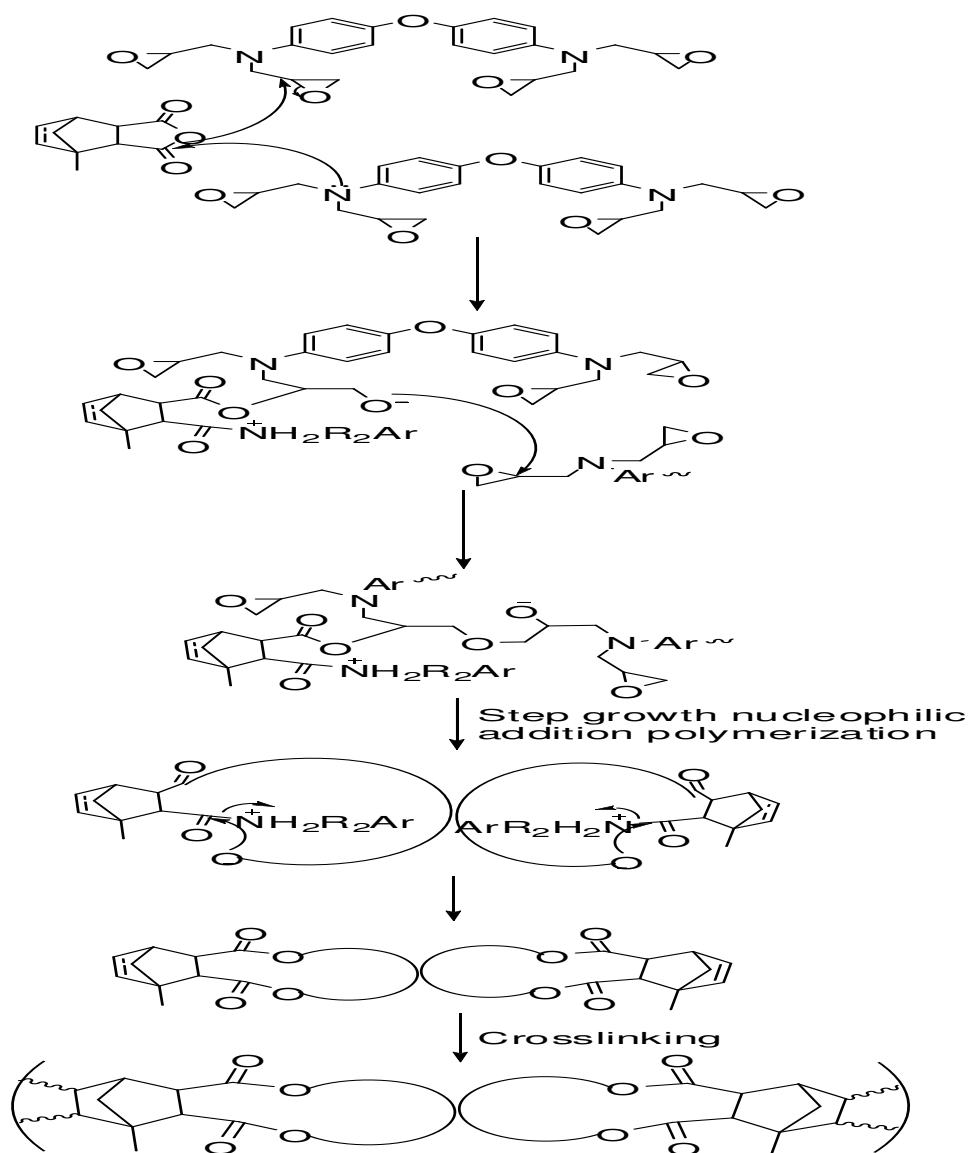
The curing behavior of the epoxy resin and curing agent composition was studied by DSC (Fig.5). The reactivity of the epoxy resin can be directly read from the exothermic starting temperature. The DSC graph of uncured epoxy/MNA for the curing procedure showed two step curing pattern (Fig.5). The onset of an exothermic peak at 150 °C depicted initiation of curing while the maximum rate of curing was observed at 177 °C. The curing of tetra-functional epoxy resin subsided at 225 °C. The first step curing pattern was observed due to opening of epoxy ring and formation of ester linkage. The second step curing process initiated at 250 °C with maximum rate of curing at 325 °C. The second step of curing was attributed due to cross linking of double bond of esterified methyl nadic anhydride. The DSC graph of cured tetra-functional epoxy resin showed the glass transition temperature at 197 °C (Fig.6).



**Fig.5:** DSC graph of uncured epoxy resin.



**Fig.6:** DSC graph of cured epoxy resin.



**Scheme-2:** Possible mechanism of polymerization.



## CONCLUSION

The tetra-functional epoxy resin has been synthesized by the reaction between diamino-diphenyl ether with epichlorohydrin under mild basic condition. The curing properties of synthesized epoxy resin have been evaluated using methyl nadic anhydride as a curing agent. The resin has been characterized by FT-IR and <sup>1</sup>HNMR spectroscopy. The curing behavior of synthesized epoxy resin has been studied using FT-IR and DSC techniques. The FT-IR analysis of uncured resin along with MNA showed characteristic peak at 1033 cm<sup>-1</sup> corresponding to C-O stretching of epoxy ring, diminished upon curing and a peak at 3500 corresponding to O-H stretching increased due to formation of free hydroxyl group by the opening of epoxide ring. The DSC analysis of uncured resin showed maximum rate of curing at 177 °C while the cured resin showed Tg at 197 °C. The TGA analysis showed two step degradation with thermal stability up to 350 °C.

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